STRUCTURAL AND ELECTRONIC PROPERTIES OF MAGNESIUM-3D TRANSITION METAL SWITCHABLE MIRRORS

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Abstract

We have observed reversible mirror-to-transparent state switching in a variety of mixed metal thin films containing magnesium and first-row transition elements including Ni, Fe, Co, Mn, and Ti. The very large changes in both reflectance and transmittance on loading these films with hydrogen are accompanied by significant structural and electronic transformations. The valence states and coordination of metal atoms during hydrogen loading were followed using dynamic in situ transmission mode X-ray absorption spectroscopy. Time-resolved Mg K-edge and Ni, Co, Mn, and Ti L-edge spectra reflect both reversible and irreversible changes in the metal environments. These spectra are compared to those of reference materials and to predictions from calculations.

Keywords: A. hydrogen storage materials, thin films; C. EXAFS, NEXAFS, X-ray diffraction.

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1. Introduction

Switchable mirror films with variable optical properties are attractive materials for regulation of light and heat transfer in buildings, vehicles, and satellites, and may have applications in sensor technologies. The first switchable mirrors based on hydrogen absorption and desorption were reported by Huiberts *et al.* [1]. Magnesium-rare earth alloy films were shown by van der Sluis *et al.* to offer improved dynamic ranges and color neutral transparent states [2]. Recently Richardson *et al.* [3,4] reported switchable mirror effects in thin films of Mg and 3d transition metals (Ni, Mn, Fe, and Co), which avoid the use of rare earth metals and may therefore be more cost effective and stable. An understanding of the chemical and physical changes occurring during switching is essential to the effort to improve the cycling stability and dynamic range of devices based upon these materials.

Near-edge x-ray absorption fine structure (NEXAFS) and extended x-ray absorption fine structure (EXAFS) are powerful tools for understanding the electronic and structural properties of thin films [5,6]. These techniques are element-specific and capable of probing the short to medium range structure around an absorbing atom. Among the experimental techniques employed in determining the valence states of atoms in solids, NEXAFS plays a crucial role due to its simplicity and universal applicability. EXAFS is sensitive to the local structure around atoms, and is especially useful in studying amorphous materials. Detailed XAS studies of hydriding behavior in Mg-transition metal films have been submitted for publication elsewhere. Here we summarize our findings for two distinct cases: Ni-Mg, in which there is alloy formation in the metallic state and a ternary hydride in the transparent films; and Ti-Mg, in which there is

little interaction between the metals and their hydrides are present as distinct binary phases.

2. Experimental

Mixed metal films for optical spectroscopy containing Mg with Ti, Mn, Fe, Co, and Ni were prepared on microscope slides by DC magnetron co-sputtering from separate 5 cm diameter targets. Table (I) shows base and process pressures, Mg and transition metal sputtering powers, and film and Pd overlayer thicknesses for these samples. Two different compositions for each system were obtained using angled co-deposition. Ten nanometer thick Pd films were deposited at 1.3 x 10^{-7} Torr base pressure, 10 mTorr Ar pressure, and 12 watts power. Optical properties in the visible and near infrared (NIR) ranges were recorded using a Perkin-Elmer Lambda 19 spectrophotometer. A specially designed sample holder allowed recording of spectra from samples blanketed by a laminar gas flow of pure Ar, 4% H_2 in Ar, or dry air. Film thicknesses were measured by stylus profilometry. Film compositions were determined by Rutherford backscattering spectrometry.

Samples for *in situ* x-ray absorption spectroscopy (XAS) were deposited on 100 nm thick Si_3N_4 membranes (Silson Ltd., Northampton, UK). In order to avoid rupturing of Mg-Ti samples during hydrogenation, they had to be coated on both sides of membrane. XAS measurements were performed on Beamline 6.3.1 at the Advanced Light Source, Lawrence Berkeley National Laboratory.

3. Results and discussion

3.1 Optical spectroscopy

The substrate transmittance was over 90% between 350 and 2500 nm and was featureless. The reflectance was about 8% with a broad minimum at ~ 2100 nm. A thin Pd overlayer is required to protect the reactive layers from oxidation and to promote dissociation and absorption of hydrogen. At ambient temperature in 4% H_2, the composition of the film is $PdH_{\sim 0.6}$ [7]. The transmittance and reflectance spectra (taken from the film and substrate sides) of a 10 nm Pd film in the virgin and hydrided states are shown in Figure 1.

3.1.1 Reflectance of co-deposited Mg-Ti, -Mn, -Fe, -Co, and -Ni films

Reflectance spectra obtained from the substrate sides of the samples (to reduce contributions from the Pd layer) are shown in Figure 2. Only the samples with higher transition metal content are shown to emphasize the differences. An increase in Mg content in each system caused an increase in reflectivity in the metallic states, but the spectral features were unchanged. The absorption peak around 2135 nm observed in Ti-Mg, Mn-Mg, and Co-Mg films disappeared on hydriding. The spectra of hydrided Ti-Mg, Mn-Mg, and Fe-Mg films were similar to one another. Residual visible reflectivity was higher in the hydrided Co-Mg and Ni-Mg systems.

3.1.2 Transmittance spectra

The visible-NIR transmittance in the metallic state was very low for all samples (Fig. 3). In the hydride state, Co-Mg and Ni-Mg films were somewhat colored due to absorptions in the visible range. The intensity of the color was directly dependent upon

Co or Ni content, consistent with the formation of the colored ternary hydrides Mg_2NiH_4 [8] and Mg_2CoH_5 [9] along with MgH_2, which is transparent across the visible spectrum [10]. A very broad maximum in transmission between 1000 and 1500 nm was present in all cases. The features at around 800 nm and 1900 nm seen in these spectra (and also in the Ni-Mg hydride reflectance spectrum) are instrumental artifacts. Higher transition metal concentrations always led to faster switching time and decreased maximum transparency.

3.2 XAS investigation

3.2.1 Mg-Ni films

In situ Ni L-edge spectra were recorded at intervals of about 5 min during hydrogen loading (Fig. 4). The small initial positive shift in the absorption edge and maxima is due to formation of the interstitial hydride [8]. This phase is then converted to Mg_2NiH_4 [8]. The intermediate spectra show the existence of a mixture of the latter two phases during the conversion. The edge shift (~2.5 eV) at the end of hydrogenation process is consistent with conversion from a metallic to a semiconducting state (e.g. Mg_2NiH_4), but somewhat larger than that predicted by *ab initio* calculation [11]. Similar changes are observed in the Mg K-edge spectra of Ni-Mg films (Fig. 5). Interaction of Mg with Ni produces some Mg_2Ni in the metallic film. The presence of hydrogen as a near neighbor around Mg in MgH_2 and Mg_2NiH_4 and the volume expansion in the hydrided film produce a drastic reduction in the intensities of multiple scattering resonances at higher energies. The Mg absorption edge also shifts by about 2.5 eV.

3.2.2 Mg-Ti films

Mg and Ti do not form an alloy under normal conditions, and no ternary hydride is known. An unexpectedly small Ti L-edge shift toward higher energy occurs during hydrogen absorption (Fig. 6), since in 4% H_2 at ambient temperature, complete conversion to TiH_2 is expected [12]. The Mg K-edge behavior (Fig. 7) is similar to that in the Ni-Mg films, except that here only Mg is seen in the metallic state and only MgH_2 in the hydrided film.

4. Conclusions

The switching mechanism in the Mg plus Ti, Mn, Fe, Co, and Ni systems studied here appears to be reversible formation of MgH_2 and, where possible, known ternary hydrides. The dramatic changes in both transmittance and reflectance in these materials are well correlated with the structural and electronic transitions observed by XAS. While hydrided Ni-Mg mixed films clearly contain binary and ternary hydrides, Ti acts primarily as a catalyst for formation of MgH_2.

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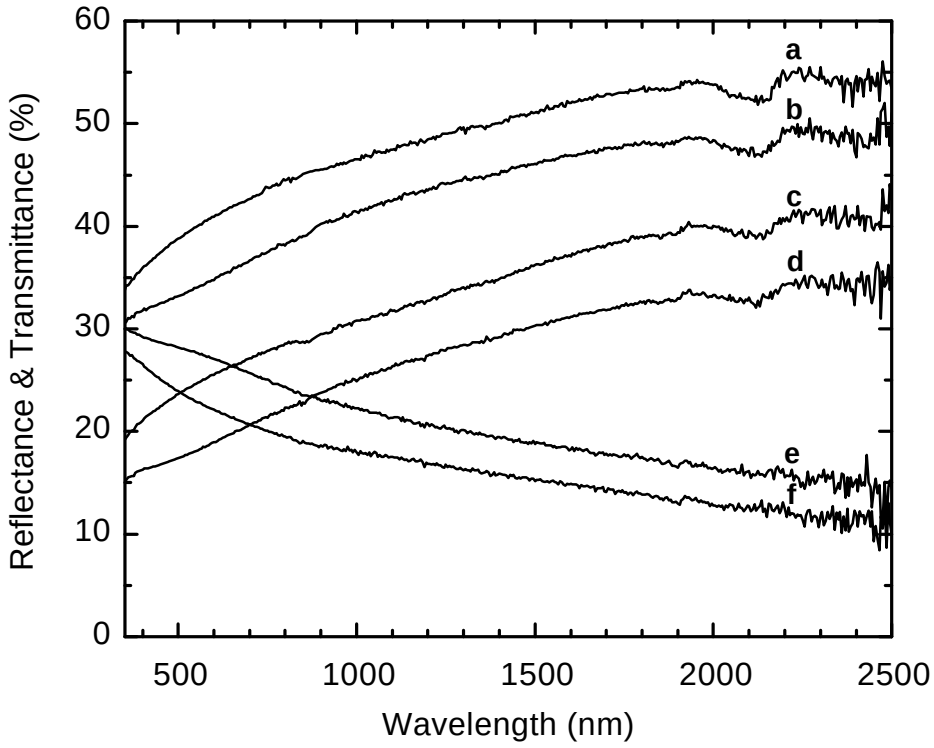
Table (I): Sputter deposition parameters.

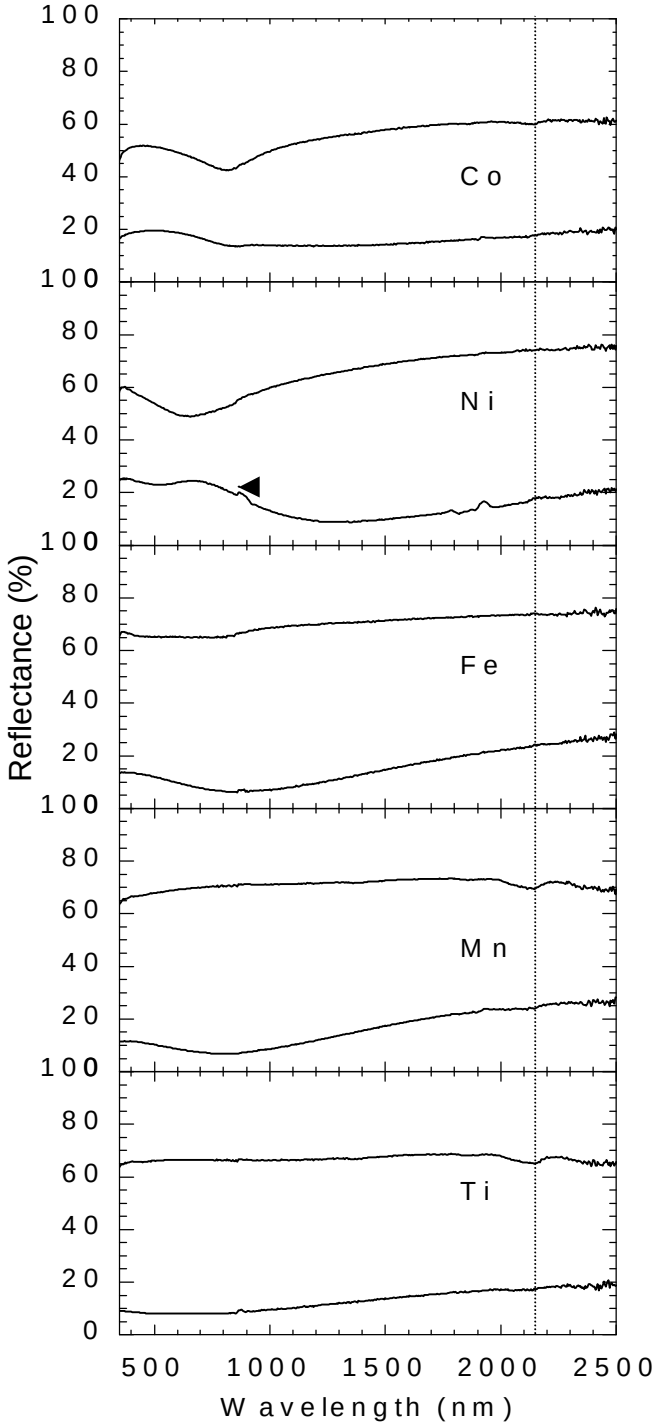
	Base Pressure (Torr)	Process Pressure (Ar) (mTorr)	3d-element Power (Watt)	Mg Power (Watt)	Composition	Film Thickness (nm)	Pd overlayer (nm)
Ti-Mg (a)	3.1×10^{-7}	2	45	40	$Mg_{0.73}Ti_{0.27}$	42	10
Ti-Mg (b)	3.1×10^{-7}	2	45	40	$Mg_{0.85}Ti_{0.15}$	53	10
Fe-Mg (a)	2.1×10^{-7}	2	29	36	$Mg_{0.63}Fe_{0.37}$	76	7
Fe-Mg (b)	2.1×10^{-7}	2	29	36	$Mg_{0.79}Fe_{0.21}$	81	7
Co-Mg (a)	1×10^{-7}	2	30	36	$Mg_{0.65}Co_{0.35}$	51	7
Co-Mg (b)	1×10^{-7}	2	30	36	$Mg_{0.79}Co_{0.21}$	62	7
Ni-Mg (a)	1.7×10^{-7}	2	25	36	$Mg_{0.78}Ni_{0.22}$	73	8
Ni-Mg (b)	1.7×10^{-7}	2	25	36	$Mg_{0.84}Ni_{0.16}$	81	8
Mn-Mg (a)	2.6×10^{-7}	2	15	40	$Mg_{0.65}Mn_{0.35}$	47	8
Mn-Mg (b)	2.6×10^{-7}	2	15	40	$Mg_{0.8}Mn_{0.2}$	62	8

Figure captions

1. Reflectance through film side in metallic (a) and hydride state (b), reflectance through substrate side in metallic (c) and hydride sate (d), and transmittance in hydride (e) and metallic state (f) of 10 nm Pd film on glass.
2. Reflectance through substrate side in metallic (upper curve) and hydride (lower curve) states of mixed transition metal-Mg films. See Table (I) for film thicknesses. The dotted line indicates absorption peaks at ca. 2135 nm.
3. Transmittance of mixed transition metal-Mg films in metallic (lower curve) and hydride (upper curve) states. See Table (I) for film thicknesses.
4. Transmission mode Ni $L_{III,II}$-edge NEXAS spectra of $Ni_{0.24}Mg_{0.76}$ thin film measured in He (denoted as 'virgin') and in 4 % H_2 in He (other curves) at ca. 5 min intervals during hydriding. The curve denoted as 'end of hydrogenation' was recorded after 24h.
5. Mg K-edge EXAFS transmission spectra of thin films in He: (a) Mg (270 nm), (b) $Ni_{0.13}Mg_{0.87}$ (232 nm), (c) $Ni_{0.33}Mg_{0.67}$ (154 nm); in 4 % H_2 (He): (d) $Ni_{0.13}Mg_{0.87}$, (e) $Ni_{0.33}Mg_{0.67}$. The dotted line at 1300 eV is an aid to the eye.
6. Ti L-edge of $Ti_{0.16}Mg_{0.84}$ film in metallic (in He) and hydride state (in 4% H_2).
7. Mg K-edge EXAFS transmission spectra of thin films in He: (a) Mg (270 nm), (b) $Ti_{0.27}Mg_{0.73}$, (c) $Ti_{0.16}Mg_{0.84}$; in 4% H_2 (He): (d) $Ti_{0.27}Mg_{0.73}$, (e) $Ti_{0.16}Mg_{0.84}$ The dotted line at 1300 eV is an aid to the eye.



Farangis et al., Figure 1



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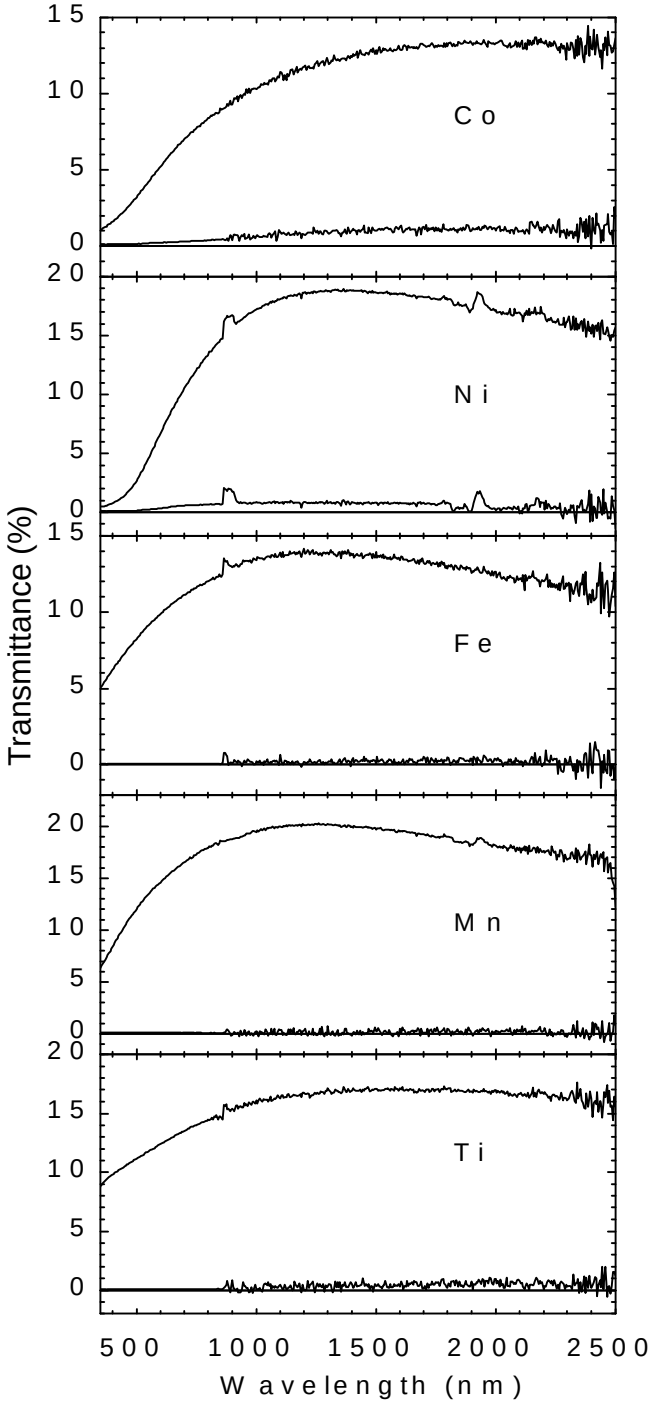

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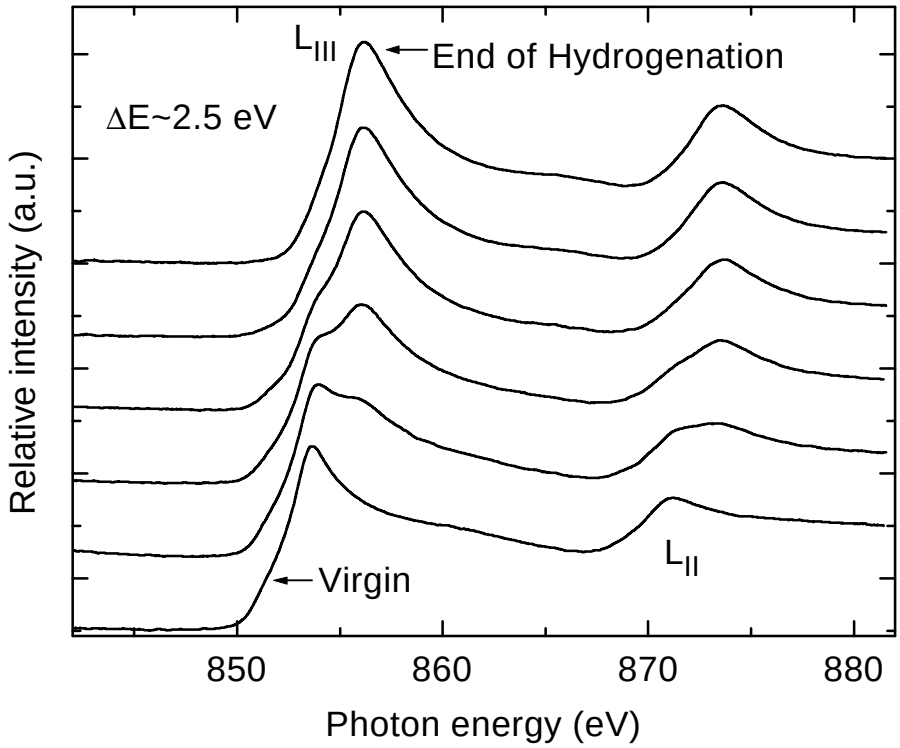

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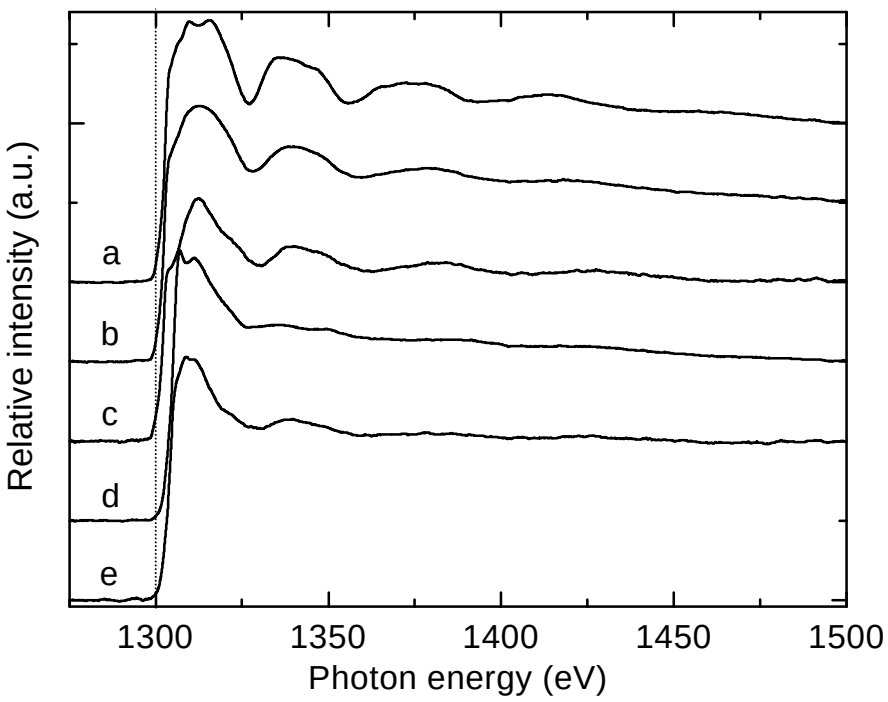

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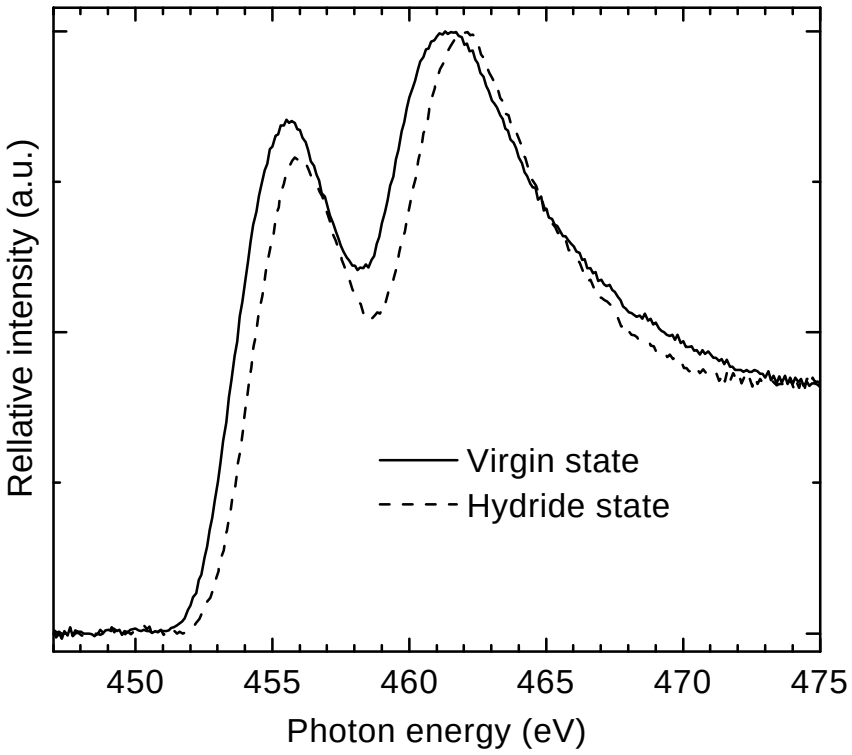

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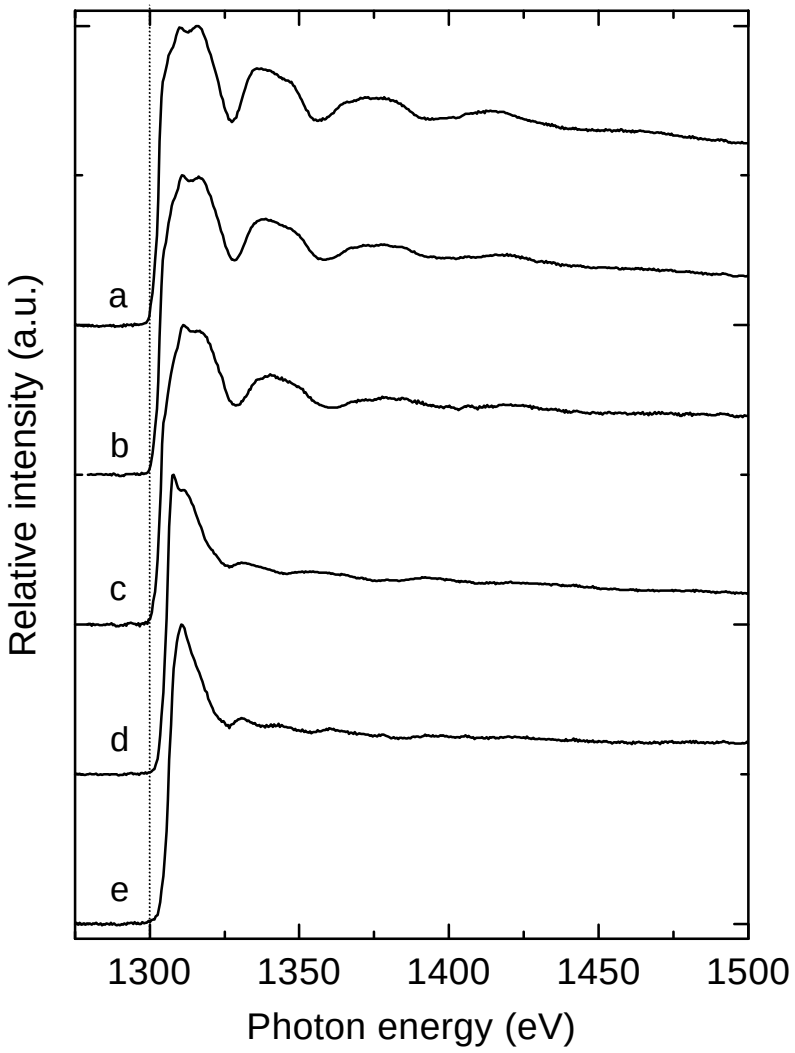

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